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TITLE:

Analysis of Chlorosulfonic Acid Scrubber for PCB's - Fate of Aroclors in Chlorosulfonic Acid.

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PERSONNEL:

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PROBLEM:

Determine efficiency of chlorosulfonic acid scrubber in removing Aroclors present in Dept. 246 off-gas.

JUSTIFICATION:

Prevent contamination of product (C/S Acid) and environment with polychlorinated biphenyls.

SUMMARY:

Our analytical data indicates that chlorosulfonic acid can be an effective scrubbing media for removing entrained organics from certain types of departmental off-gases. The effectiveness of a C/S acid scrubber has been shown to be due to its ability to sulfonylate a variety of aromatic compounds including chlorobenzenes, chlorophenols and chlorinated biphenyl. The reaction gives basically sulfonyl chlorides of such compounds, however, in some cases aromatic sulfones might be formed.

A reaction between Aroclor 1242 and chlorosulfonic acid has been demonstrated and the principal products identified as sulfonyl chlorides. The derivatives obtained were solid of limited solubility in water and assumed to have very low volatilities. Their stability and toxicity in the environment, compared to the parent polychlorinated biphenyls, is not known at this time but should be considered prior to disposal of large amounts for extended periods.

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Details

Background

Calculations based on available analytical data indicates that polychlorinated biphenyls (PCB's) are present in department 246 (Aroclor) off-gas at about a 30 ppm level. When not sewered, this HCl gas is passed to department 217 for chlorosulfonic (C/S) acid production. The inlet gas is initially scrubbed with C/S acid to remove entrained PCB's. The spent scrubber is also discharged to the sewer at intervals.

An analysis of the spent scrubber acid was needed to establish efficiency and determine the contribution to sewer contamination at the time of disposal. As a result of the analysis of a sample of "4-hour old" acid from the No. 300 scrubber, additional analytical work was undertaken to establish the fate of Aroclor introduced into C/S acid.

This report covers the analytical examination of a C/S acid scrubber sample, and subsequent work to define the fate of Aroclors added to chlorosulfonic acid.

Experimental

A. Analyses of C/S Acid Scrubber

Preparation for Analyses

The organic matter present in the C/S acid sample was isolated as hexane extractables by extracting the aqueous hydrolyzate of the acid with solvent. A 25 gram sample was added, under carefully controlled conditions in a specially prepared hydrolysis apparatus, to about 250 mls of ice-water. The hexane extracts of the hydrolyzate were collected for analysis.

Analytical

A quantitative examination of the hexane solution for PCB's was made following our standard PCB analytical procedure. The analysis was concluded by electron capture gas chromatography (EC/GC).

The oily, viscous residue remaining after evaporation of the hexane was subjected to both infrared and conventional gas chromatographic analyses. Specific derivatization techniques were subsequently employed to verify the presence of prominent chemical classes indicated by the infrared absorption spectra. Analyses of the derivatization reactions or products were made by gas chromatography and infrared.

B. Simulated C/S Acid Scrubber

Preparation and Sampling

A sample of sales-grade C/S acid was prepared containing 360 ppm PCB's as Aroclor 1242. This concentration approximates the

level that was assumed to have been introduced into the actual scrubber via off-gas scrubbing. The simulated scrubber acid was allowed to stand at room temperature (25°C). A 25 gram sample was taken at 4 hours after contamination and again after 48 hours.

Analytical

The "4-hour old" sample was immediately hydrolyzed and a quantitative analysis for PCB's carried out as described above. The hydrolyzate of the 48-hour sampling was also examined for PCB's. In addition an infrared absorption analysis was made on a solid residue obtained following the evaporation of the hexane solvent.

Results and Discussion

A. Analyses of Scrubber Sample

No detectable amount of PCB's were found in the No. 300 scrubber sample. Based on the sample size used and the related chromatographic conditions, the lower detection limit was of the order of 100 ppb. The anticipated level was in the parts per million range (~250 ppm). Two separate samplings were made, including one from an apparent sedimentation layer at the bottom of the sample container.

An oily, viscous residue isolated after solvent removal represented ~0.5% (vol./wt.) of the spent acid. Infrared and conventional GC analyses indicated the oil to be a complex mixture with a wide range in volatility. Interpretation of the strong or significant bands of the infrared spectrum suggested a mixture of aromatic, sulfonyl chloride-type compounds of different origins.

The attached table of analytical data reports the presence of some compounds of a phenolic origin. This was substantiated by the altered elution times of several peaks when comparing chromatograms before and following the reaction of a portion of the isolate with a silylating reagent. The reagent used, reacts readily with most phenolics to form silyl ethers having altogether different GC elution characteristics than the parent phenols. In assessing the combined analytical data, it would appear that some volume of off-gas from dept. 236 - and perhaps 233 - have also been introduced into the scrubber.

To verify that the major identifying characteristic of the isolated organic matter was that of an aryl sulfonyl chloride, its reaction to gaseous ammonia was evaluated by infrared absorption analysis. The reaction with NH_3 proceeds according to the equation:

$$ArSO_2Cl + 2\ NH_3 \longrightarrow ArSO_2NH_2 + NH_4Cl$$

yielding an aryl sulfonamide (Ref. 1). The two infrared absorption bands of the common $-SO_2-$ group shifts from approximately 1370

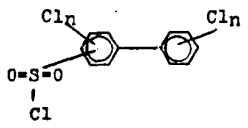
and 1175 cm^{-1} in sulfonyl chlorides to about 1320 and 1150 cm^{-1} in the sulfonamide (Ref. 2).

Addition of NH_3 to a benzene solution of the oily mixture resulted in a solid derivative having major absorption bands at the sulfonamide absorption frequencies. The observed shifting of the major band frequencies from 1375 to 1325 cm^{-1} and 1175 to 1155 cm^{-1} confirmed that the organic matter isolated from the spent scrubber was predominantly a mixture of aryl sulfonyl chlorides.

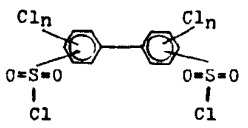
B. Fate of Aroclor in C/S Acid

The results of the preceeding analytical work on the spent scrubber indicated that most of the aromatics entering the scrubber were reacting to form sulfonyl chloride derivatives. Since the identifying data was somewhat general and not necessarily specific with respect to the fate of Aroclor, a sample of sales-grade acid was "doped" with 1242 and examined at specified intervals.

Four hours after contamination of the acid, no detectable quantity of PCB's were found in the hexane extract of the hydrolyzate. The sulfonylation of Aroclor 1242 was essentially proven, when strong bands of the $-SO_2-$ group were observed in the infrared spectrum of the solid residue obtained at the 48 hour sampling. The type of structures indicated from the reaction products are:



and



where n = ≥ 1

It is apparent that steric hinderance would prevent the highly chlorinated isomers from reacting. A separate EC/GC examination was made, but failed to provide any clear-cut information in this regard. It is assumed that for 1242 all major isomers were sulfonylated to some degree.

Conclusions

Our analytical data indicates that chlorosulfonic acid can be an effective scrubbing media for removing entrained organics from certain types of departmental off-gases. The effectiveness of a C/S acid scrubber has been shown to be due to its ability to sulfonylate a variety of aromatic compounds including chlorobenzenes, chlorophenols and chlorinated biphenyl. The reaction gives basically sulfonyl chlorides of such compounds, however, in some cases aromatic sulfones might be formed.

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References

1. R. L. Shriner, R. C. Fuson, "Identification of Organic Compounds", 3rd Vol. Wiley, New York, N. Y. 1948.

2. N. B. Colthup, et al, "Introduction to Infrared and Raman Spectroscopy", Academic, New York, N. Y. 1964.

3. Laboratory Notebook, 16101-16200, 16140.

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Summary - Analytical Data

Sample	Description	Analytical
Dept. 217 - No. 300 C/S Acid Scrubber	4-hour old Brown-Black color	EC-gas chromatography: No detectable amount of PCB (2) Conventional - GC: Series or groups of peaks eluting up to 3 hrs. Infrared: Strong bands at 1375 and 1175 cm^{-1} found in isolate, indicative of $-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-Cl$ group (sulfonyl chloride) Aromatic ring(s) absorption ~3065 cm^{-1} Minor absorption band at 3475 cm^{-1} indicates possible presence of small amounts of phenolics
Lab Prepared- sales grade C/S with 360 ppm of 1242 added	4-hour old (1)	EC/GC: No detectable amount of PCB (2)
	48-hour old(1)	EC/GC: No detectable amount of PCB (2) Infrared Isolated solid matter gave strong bands @ 1370 and 1174 cm^{-1} indicative of sulfonyl chloride group

(1) - Sample showed slight but definite discoloration
(2) - EC/GC lower detection limit = 100 ppb

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